PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : D21C 9/147

A1

(11) International Publication Number: WO 97/17489

(43) International Publication Date: 15 May 1997 (15.05.97)

(21) International Application Number: PCT/SE95/01335

(22) International Filing Date: 9 November 1995 (09.11.95)

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(81) Designated States: AL, AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published
With international search report.
In English translation (filed in Swedish).

(54) Title: PROCESS FOR OXYGEN DELIGNIFICATION

(57) Abstract

A method of oxygen-gas delignifying chemical pulps, wherein the oxygen-gas delignification process is carried out at an oxygen-gas pressure above 10 bars. According to one preferred embodiment, the oxygen-gas delignification process is carried out at an oxygen-gas pressure from 15 bars, preferably at 15-20 bars. The oxygen-gas delignification process is carried out on non-bleached pulp or on pulp that is first subjected to oxygen-gas delignification and optionally also to ozone delignification. The pulp may also have been treated with a chelating agent in at least one position in the process.

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PROCESS FOR OXYGEN DELIGNIFCATION

The present invention relates to a method for the oxygen-gas delignification of chemical pulp. More specifically, the invention relates to the oxygen-gas delignification of chemical pulp at high oxygen-gas pressures.

Oxygen-gas delignification is one of the methods used within the pulp industry to remove lignin from the pulp prior to the final bleaching stage. The method has increased in significance, because the soluble substances that are formed in the oxygen-gas delignification process are returned and burned and therewith do not result in toxic secondary products in the waste water from the bleaching department. The interest in oxygen-gas delignification has led to comprehensive studies in research laboratories around the world. However, there is still a desire to achieve improved process performances.

Oxygen-gas delignification of chemical pulp is typically carried out on an industrial scale at a pressure of about 5 bars. The pressure is normally restricted to 5-10 bars in laboratory work. This also applies to work in which the influence of the pressure on the delignification process has been studied *per se*. Those experiments that have been reported in the literature give no indication that a pressure above 10 bars would afford any advantage. L. Olm, A. Teder, TAPPI 1979 Pulping Conference, Seattle, pp. 169-179, has studied the kinetics of oxygen-gas delignification, one of the variables being the partial pressure of oxygen-gas. The effect of the oxygen-gas pressure on the rate of delignification and on selectivity has been examined. Selectivity is a measurement of viscosity decrease per decrease in kappa number. The boundary viscosity of the pulp is a measurement of the degree of polymerization of the cellulose and thus provides an indication of pulp quality. It was found that the delignification rate increased when the oxygen-gas

pressure increased from 1 to 10 bars. However, the greatest increase was observed at the lower pressures, between 1 and 5 bars, and the increase progressively tapered off at pressures from 5 bars up to 10 bars. Extrapolation of these results indicates that no appreciable increase in the rate of delignification can be expected at oxygen-gas pressures above 10 bars. With regard to selectivity, L. Olm, A. Teder found that the oxygen-gas pressure had no effect at all.

However, it has surprisingly been found, in contradistinction to the data published in the literature, that oxygen-gas delignification at pressures higher than conventional pressures results in considerably enhanced delignification and, in many cases, in a retained or improved selectivity. The effect can be utilized to obtain either more extensive delignification or to maintain delignification at a reduced stay time or residence time in the oxygen-gas stage. It is found that at retained delignification, the boundary viscosity of the pulp is equal to that, or in certain cases better than that obtained with conventional pressures, i.e. selectivity is retained or improved at the higher pressure.

As will be evident from the following Claims, the present invention thus provides an improved method for the oxygen-gas delignification of chemical pulp, in which oxygen-gas delignification is effected at oxygen-gas pressures above 10 bars. According to one preferred embodiment of the invention, the oxygen-gas delignification is effected at oxygen-gas pressures ranging from 15 bars, most preferably between 15-20 bars. It is unnecessary to define an upper limit for the oxygen-gas pressure, since the method will function well at still higher pressures. The upper limit is governed rather for reasons of a process-technical and economical nature.

It has also been found that the same good effect is provided by the inventive method irrespective of the

delignification techniques used after the cook. Good results are achieved when oxygen-gas treating unbleached pulp, and good results are also achieved when delignifying pulp that has already been oxygen-gas delignified or when delignifying oxygen-gas and ozone delignified pulp. The results achieved with oxygen-gas delignification and ozone bleaching are improved generally when the heavy metal content of the pulp can be kept low. Treatment with chelating agents or complex builders is possible in different positions in the process, for instance prior to a first oxygen-gas stage, prior to a second oxygen-gas stage and prior to an ozone-bleaching stage. An addition of hydrogen peroxide can be used in the oxygen-gas delignification process. It can be assumed to be highly probable that the good effect afforded by the invention will also be obtained when using other delignification techniques after the cook. There can be mentioned by way of example hydrogen peroxide, peracetic acid, Caros acid, different enzymes (xylanases, mannanases, laccases, peroxidases) and chlorine dioxide. By chemical pulp is preferably meant sulphate pulp, soda pulp, sulphite pulp and organosol pulps or pulps deriving from other solvent-based cooking methods.

According to known techniques, oxygen-gas delignification of the chemical pulp is carried out in the presence of sodium hydroxide at controlled conditions with respect to pulp consistency, treatment times, treatment temperature and final-pH. Conventional conditions are applied when carrying out the present invention, with the exception of the high oxygen-gas pressure. Thus, the inventive method is carried out conveniently at a pulp consistency of 5-50%, preferably 8-15%. The temperature is controlled to levels between 70-130°C, preferably 90-110°C. The treatment time may vary from fifteen minutes to three hours, although a preferred treatment time is between thirty minutes to ninety minutes. The amount of causttic liquor or alkali introduced to the system may

also vary within wide limits, depending on pulp type differences, cooking conditions, etc. The amount of liquor charged may vary from 5-50 kg/ton, preferably 10-25 kg/ton. The final pH of the pulp is normally controlled to lie between 8-12, preferably 10-11. In oxygen-gas delignification processes, magnesium sulfate is often also added to the pulp, in addition to alkali. The magnesium sulfate is conveniently added in an amount corresponding to 0-10 kg/ton, preferably 2-5 kg/ton.

When applying the inventive method on pulp that has already been oxygen-gas delignified, the pulp is first treated with a chelating agent, or complex builder, such as EDTA, in a so-called Q-stage. The pulp is then subjected to oxygen-gas delignification in accordance with the invention, as described above. The method can also be applied with pulp that has previously been treated with a chelating agent in at least one position in the process, for instance a pulp that has been treated in solely one Q-stage without being oxygen-gas deligni fied previous thereto. According to another embodiment of the invention, the pulp is treated with oxygen-gas and peroxide at high pressure subsequent to the Q-treatment.

The invention will now be illustrated with reference to a non-limiting example.

<u>Example</u>

Two different non-bleached softwood sulfate pulps were used in the tests. One pulp had a kappa number of 29.3 and a viscosity of 1220 dm^3/kg, and the other had a kappa number of 15.8 and a viscosity of 1095 dm^3/kg.

Magnesium sulfate and alkali (NaOH) were added to the pulp at room temperature and mixed in the pulp at a 12% pulp consistency. The pulp was then placed in steel autoclaves and oxygen-gas was supplied to achieve the desired oxygen-gas pressure. The autoclaves were placed in a rotary stand in an air bath. The autoclaves were heated to 105°C and a time count was started. At the end

of a desired bleaching time, the autoclaves were removed from the bath and the pressure released, whereafter the autoclaves were cooled in water. The final-pH was determined. The pulp was washed and then analyzed with respect to kappa number and viscosity.

Further tests were carried out on two different oxygen-gas delignified softwood sulfate pulps, wherein one pulp had a kappa number of 12.7 and a viscosity of 1090 dm^3/kg and the other had a kappa number of 11.7 and a viscosity of 1080 dm^3/kg. Tests were also carried out on an oxygen-gas delignified softwood sulphite pulp having a kappa number of 10.7 and a viscosity of 985 dm^3/kg.

The pulps were placed in plastic bags and chelating agent (EDTA) and sulphur dioxide (SO_2) were admixed with the pulp at a 10% pulp consistency. The pulps were removed after 60 minutes at a temperature of 70°C and the final-pH determined. The pulps were washed.

In some cases the pulp was delignified with ozone after treating the pulp with the chelating agent. The pulp was placed in a titanium mixer for laboratory use. The pulp was fluidized with the aid of a rapidly rotating turbine, whereafter ozone was metered quickly from a pressure vessel. After a fluidizing period of twenty seconds, the pulp was allowed to lie for five minutes with no mixing. The pulp was removed, the final pH determined and the pulp washed at a pH of about 7. Finally, there was used a softwood sulfate pulp which had been delignified in two previous oxygen-gas stages and thereafter treated with a chelating agent (EDTA) and sulphur dioxide. The pulp had a kappa number of 9.0 and a viscosity of 895 dm^3/kg.

The oxygen-gas delignification process was carried out in the same way as that described above with reference to non-bleached sulfate pulps. The bleaching conditions for the different tests are shown below in Table 1, where Q-stage (chelating agent) and Z-stage (ozone) were only applied in certain tests (see result

Tables).

Table 1.

	O-stage (oxygen gas)	Q-stage (chelating agent)	Z-stage (ozone)	(OP-stage) (oxygen gas/per-oxide)
Const. %	12	10	10	12
Temp. °C	105	70	45	100
Time min.	30-60	60	5	120
Charges kg/ton	NaOH:10-25 $MgSO_4$: 5 O_2:7-20bars	EDTA: 2 SO_2: 5	Z: 3	NaOH:15-20 H_2O_2:20-30 O_2:7-20bar
Final pH	10-11	5-6	2-3	10.5-11.5

Results of non-bleached pulp.

Table 2. Non-bleached softwood sulfate pulp - oxygen-gas delignification at 15 bars.

Kappa No.: 29.3 Viscosity: 1220 dm^3/kg

Pressure bars	Alkali charge NaOH kg/ton	Time min.	Final pH	Kappa No.	Viscosi-ty dm^3/kg
7 (ref)	20	60	10.9	16.7	1080
15	20	60	9.7	15.0	1080

Comparisons between O-stages at conventional 7-bar pressure shows that the pulp is delignified more quickly and to a greater extent at the higher pressure (Table 2) and with the same alkali charge. The lower kappa number is achieved with retained viscosity, i.e. selectivity is improved.

Table 3. Non-bleached softwood sulfate pulp - oxygen-gas delignification at 20 bars.

Kappa No.: 25.8 Viscosity: 1095 dm^3/kg

Pressure bars	Alkali charge NaOH kg/ton	Time min.	Final pH	Kappa No.	Viscosity dm^3/kg
7 (ref)	15	40	10.1	7.8	980
7 (ref)	20	40	11.0	7.0	945
7 (ref)	20	50	10.9	6.8	930
20	15	40	9.7	6.7	930
20	20	30	10.5	6.0	910
20	20	40	10.1	5.7	890

When making a comparison between the pressures of 7 bars (reference) and 20 bars, it was found that delignification was increased by an amount corresponding to slightly more than one kappa number unit at the higher pressure (Table 3) with identical alkali charges and time. When the delignification processes were continued for equal lengths of time, the viscosities were mutually the same, which showed that the selectivity had been maintained.

Results of tests on oxygen-gas delignified pulp.

Table 4. Oxygen-gas delignified softwood sulfate pulp - oxygen-gas delignification at 15 bars.

Kappa No.: 12.7 Viscosity: 1090 dm^3/kg
Sequence: OQO

Pressure bars	Alkali charge NaOH kg/ton	Time min.	Final pH	Kappa No.	Viscosity dm^3/kg
7 (ref)	14	60	10.5	7.5	970
15	14	60	10.2	7.0	990

In tests using pressure of 7 bars (reference) and pressure of 15 bars, the higher pressure resulted in a lower kappa number and higher viscosity at identical alkali charges and time (Table 4). Delignification was thus both more effective and more selective.

Table 5. Oxygen-gas delignified softwood sulfate pulp - oxygen-gas delignification at 20 bars.

Kappa No.: 11.7 Viscosity: 1080 dm^3/kg
Sequence: OQO

Pressure bars	Alkali charge NaOH kg/ton	Time min.	Final pH	Kappa No.	Viscosity dm³/kg
7 (ref)	10	30	10.9	8.1	985
7 (ref)	15	30	11.8	7.1	955
7 (ref)	15	60	11.2	6.4	950
20	10	30	10.4	7.2	980
20	15	40	11.0	5.8	930

A comparison between the pressures of 7 and 20 bars showed an increased delignification corresponding to about one kappa number unit at the higher pressure (Table 5). The delignification could be continued to a lower kappa value of one kappa number unit with the same final viscosity.

The bleaching time required to obtain the same degree of delignification with a given quantity of alkali (15 kg/ton) at the 20-bar pressure was only about half the bleaching time required at the 7-bar pressure.

<u>Table 6</u>. Softwood sulfite pulp was delignified in an oxygen-gas stage - oxygen-gas delignification/peroxide bleaching at 20 bars.

Kappa No.: 10.7 Viscosity: 985 dm^3/kg

Sequence: OQ(OP)

Pressure	Alkali charge NaOH kg/ton	Peroxide charge H_2O_2 kg/ton	Time min.	Final pH	Kappa No.	Viscosity dm^3/kg	Brightness % ISO
7	25	20	120	11.5	4.4	1010	85.6
20	25	20	230	11.3	3.7	930	87.7

A comparison between the (OP) stages at a conventional pressure of 7 bars and a pressure of 20 bars showed a lower kappa number at the higher pressure. The lower kappa number at the pressure of 20 bars was accompanied with a higher pulp brightness.

Result of tests on ozone-delignified pulp.

Table 7. Oxygen-gas delignified and ozone-delignified softwood sulfate pulp - oxygen-gas delignification at 15 bars.

Kappa No.: 12.7 Viscosity: 1090 dm^3/kg
Sequence: OQZQO, 5 kg $MgSO_4$/ton were added in the Q-stage.

Pressure bars	Alkali charge NaOH kg/ton	Time min.	Final pH	Kappa No.	Viscosity dm^3/kg
7 (ref)	14	60	10.6	5.7	895
15	16	60	10.7	5.2	875

A comparison between the O-stages at the conventional pressure of 7 bars and the pressure of 15 bars showed that much more alkali was consumed at the higher pressure with the same final pH, wherein the reaction proceeds more rapidly and therewith results in a lower kappa number after the same time period (Table 6). The lower kappa number was accompanied with a slightly lower viscosity. Selectivity was equally as good in both cases.

Result of tests on pulp delignified in two oxygen-gas stages.

Table 8. Softwood sulfate pulp delignified in two oxygen-gas stages.

Kappa No.: 9.0 Viscosity: 895 dm^3/kg

Sequence: OOQQ(OP)

Addition of 5 kg p/ton in the second oxygen-gas stage.

5 kg $MgSO_4$ were charged in the (OP)-stage.

Pressure bars	Alkali charge NaOH kg/ton	Peroxide charge H_2O_2 kg/ton	Time min.	Final pH	Kappa No.	Viscosity dm^3/kg	Brightness % ISO
7	15	30	120	10.6	5.5	830	83.8
20	15	30	120	10.5	5.1	835	85.0

A comparison between the (OP)-stages at a conventional pressure of 7 bars and a pressure of 20 bars showed a lower kappa number and a higher viscosity at the higher pressure. Selectivity was therewith better at the

20-bar pressure.

The lower kappa number obtained at the pressure of 20 bars was accompanied with a higher pulp brightness.

The results obtained showed clearly that oxygen-gas delignification carried out at the pressures proposed in accordance with the invention markedly accelerated delignification in comparison with conventional pressures. This effect was achieved irrespective of whether the treatment was carried on non-bleached softwood sulfate pulp, an oxygen-gas delignified pulp or an oxygen-gas delignified and ozone-delignified pulp. The selectivity was also improved when high pressures were used in a first, a second or a third oxygen-gas stage in tests carried out on softwood sulfate pulp. The effect of high pressure could then be used either to extend delignification with retained viscosity or to obtain higher viscosity at given delignification.

CLAIMS

1. A method of oxygen-gas delignifying chemical pulp, **characterized** by carrying out oxygen-gas delignification at an oxygen-gas pressure above 10 bars, a pulp consistency of 5-50%, preferably 8-15%, a temperature between 70-130°C, preferably 90-110°C, a treatment time from fifteen minutes to three hours, preferably between thirty minutes to ninety minutes, and a final-pulp pH between 8-12, preferably 10-11.

2. A method according to Claim 1, **characterized** by carrying out oxygen-gas delignification at an oxygen-gas pressure from 15 bars.

3. A method according to Claim 1, **characterized** by carrying out the oxygen-gas delignification process at an oxygen-gas pressure of 15-20 bars.

4. A method according to any one of Claims 1 to 3, **characterized** by carrying out the oxygen-gas delignification process on non-bleached pulp.

5. A method according to any one of Claims 1-3, **characterized** by oxygen-gas delignifying a pulp that has first been subjected to oxygen-gas delignification.

6. A method according to Claims 4 and 5, **characterized** by also subjecting the pulp to ozone delignification.

7. A method according to any one of Claims 4 to 6, **characterized** in that the pulp had earlier been treated with a chelating agent in at least one position in the process.

8. A method according to any one of Claims 1 to 7,

characterized by treating the pulp prior to the oxygen-gas delignification process with one or more of the chemicals hydrogen peroxide, peracetic acid, Caros acid, chlorine dioxide or different enzymes such as xylanases, mannanases, laccases or peroxidases.

9. A method according to any one of Claims 1 to 8, **characterized** in that the pulp is comprised of sulfate pulps, soda pulps, sulfite pulps and organosol pulps, or pulps deriving from cooking methods based on other solvents.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE 95/01335

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: D21C 9/147
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: D21C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	CA 897361 C (SAMUEL E. MALLETT), 11 April 1972 (11.04.72), page 6 --	1,4-5,9
A	SE 335053 B (MO OCH DOMSJÖ AB), 10 May 1971 (10.05.71), claims 1,2,4 --	7
A	EP 0386888 A2 (C-I-L INC.), 12 Sept 1990 (12.09.90), page 13, line 53 - line 58, claims 2, 4 --	6,8

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
12 June 1996	13 -06- 1996
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE 95/01335

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5091054 A (MEIER ET AL), 25 February 1992 (25.02.92), claims 11,22 -- --------	8

INTERNATIONAL SEARCH REPORT

Information on patent family members

01/04/96

International application No.
PCT/SE 95/01335

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